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# EFFECTS OF REDUCED USE OF LEAD IN GASOLINE ON VEHICLE EMISSIONS AND PHOTOCHEMICAL REACTIVITY

By

A. P. Altshuller

Director

Division of Chemistry and Physics

ENVIRONMENTAL PROTECTION AGENCY
National Environmental Research Center
Research Triangle Park, N. C.

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# EFFECTS OF REDUCED USE OF LEAD IN GASOLINE ON VEHICLE EMISSIONS AND PHOTOCHEMICAL REACTIVITY

A. P. Altshuller

A program for reduction of lead from gasoline should have the following positive environmental aspects:

1. Provide a lead-free gasoline for use with catalytic control system on 1975 and subsequent model vehicles.

2. Provide a schedule for reduction of lead compatible with achieving acceptable atmospheric levels of lead particulate material in a reasonable time interval.

3. Minimize changes in fuel composition that may lead to undesirable increases in other pollutants such as polynuclear aromatic hydrocarbons and in photochemical reactivity.

These results should be accomplished with minimal adverse impact in the following economic considerations:

1. Increase in price per gallon to consumer
2. Minimize and smooth out investment costs
3. Minimize crude oil increase
4. Minimize and smooth out process industry construction activity.

The requirement is for optimizing the environment impact at the minimal economic cost to the community.

As indicated above, reduction in lead in fuel results in increases in aromatic content to maintain octane number. Increases in aromatics in fuel have been associated in some studies with increasing polynuclear aromatic hydrocarbons in exhaust emissions and increased atmospheric photochemical reactivity. Although increases in the aromatic content

of gasoline are not the sole means of maintaining octane requirement, it appears to be the only practical means of reaching this objective rapidly. The rate and amount of increase in aromatic content will be determined by the selection of a schedule for removal of lead additives from gasoline. With respect to the effects of aromatics the rate of removal of lead additives from each grade of gasoline is particularly significant as related to the use of these grades in sub-groups of the vehicle population. These sub-groups may be categorized as follows:

1. Uncontrolled vehicles - 1967 model year and earlier models (1965 model year and earlier models in California).

2. 1968 to 1970 model year vehicles with control devices.

3. 1971 to 1974 model year vehicles requiring lower octane gasoline and equipped with evaporative control systems.

4. 1975 model year and later vehicles.

Presently available experimental results on prototype vehicles indicate that the hydrocarbon emissions including aromatic hydrocarbons will be extremely low and little influenced by the aromatic content of the fuel for 1975 model year and later vehicles. For 1971 through 1974 model year vehicles the combination of evaporative control devices, efficient first generation tailpipe emission control devices and lean mixture operation should tend to minimize effects of aromatic content of fuels. The use of tailpipe emission control devices provided significant reductions in effects of aromatic content of emissions from 1968 to 1970 vehicles compared to 1967 and earlier model vehicles.

## Fuel Composition and Vehicle Polynuclear Aromatic Hydrocarbon Emissions

Emission requirements for hydrocarbons based on Federal Standards if normalized to 1.0 for 1967 and earlier models, result in emission factors of 0.3 for 1968-1969 model vehicles, 0.2 for vehicles through 1974 and 0.02 for 1975 and later vehicles. The polynuclear aromatic hydrocarbon emissions of 1968-1970 vehicles with emission controls using several fuels average 30% of the emissions of uncontrolled 1964 to 1966 vehicles based on the work of Hoffman, et al[1] and Gross[2]. The polynuclear aromatic hydrocarbon (PNA) emissions of 1971 and later vehicles are assumed to follow the control of hydrocarbons and carbon monoxide.

The influence of fuel composition particularly aromatic content, has been investigated by both Hoffman, et al[1] and Gross[2]. Both studies agree on an increase in PNA emissions in uncontrolled vehicles with increasing aromatic content of fuel. Hoffman and co-workers reports a linear relationship between aromatics in fuel and PNA in emissions. Gross[2] indicates a decreasing sensitivity to aromatics in fuel of PNA in exhaust comparing results from 1966, 1968, and 1970 vehicles. In work reported by Gross[2] the PNA emissions from a 1970 vehicle actually decreased with increase in fuel aromatics. This result was attributed to the adverse effect of leaded deposits on PNA emissions. As a consequence, an unleaded high aromatic fuel operated with a vehicle with unleaded deposits can lead to lower PNA emissions than a lower aromatic leaded fuel operated in a vehicle with leaded deposits. Thus, the sensitivity of 1968 and later model year vehicles PNA emissions to fuel aromatic content is not resolved.

Computations have been carried out using the Bonner and Moore Study[3] results on the economic analysis of proposed schedules for removal of leaded additives from gasoline. Schedules A, O, and N were selected as the less severe schedules considered which would result in lead reduction with lesser effects on investment costs, added cost per gallon, crude oil demand, and process industry construction activity. The lead reductions proposed for the three schedules were as follows:

Selected 1971 Bonner and Moore Lead Reduction Schedules

(% Removal Over 1970-1971 Usage)

| Schedule | 1971 | 1972 | 1973 | 1974 | 1975 | 1976 | 1980 |
|---|---|---|---|---|---|---|---|
| A | 15 | 15 | 15 | 15 | 17 | 20 | 50 |
| O | 0 | 21 | 33 | 45 | 59 | 63 | 77 |
| N | 0 | 59 | 59 | 73 | 84 | 88 | 91 |

The computations consider the PNA emissions from the vehicle populations as the aromatic contents of the 93 RON, and 100 RON blends varied with schedule and year. Two sub-models were utilized, one assumed a linear variation on PNA emissions with aromatic content of the fuel blends for 1974 and earlier model years. The second sub-model considered that a significant aromatic sensitivity exists for only 1967 and earlier uncontrolled vehicles. The distribution of vehicle population was obtained assuming the available U. S. distribution pattern from 1971 vehicles back would hold throughout the 1970's. The distribution would be as follows: current year, 11%; 1 year old, 10%; 2 years old, 10%; 3 years old, 10%; 4 years old, 9%, 5 years old, 9%; 6 years old, 8%; 7 years old, 7%; 8 years old, 6%; 9 years old, 5%; 10 years old, 4%; older vehicles,11%. The results obtained from this distribution did not differ significantly from a California vehicle distribution pattern also available. (Table I)

Schedule A provides a lead-free fuel for 1975 vehicles, but does little towards removal of lead from gasoline through 1976. The schedule is such that a small initial increase of polynuclear aromatics occurs, but this is adjusted so that there is no net change compared to the reference schedule by 1973 followed by a small decrease in computed PNA emissions after 1974 compared to the reference schedule.

Schedule O provides a lead-free gasoline by 1975, but also provides for increasingly large removals of lead in the 1972 to 1975 period. This schedule provides a net decrease in computed PNA emissions in 1972 to 1976, largely because of the reduction in aromatic content of the 100 RON fuel used by the high-emission level older vehicles requiring this fuel.

Schedule N provides for an almost immediate large reduction in the lead content of gasoline with additional almost complete removal by the late 1970's. The severity of schedule N is such as to increase aromatic content in the three grades of gasoline so as to cause a sizable increase in computed PNA emissions over the reference schedule. The increase becomes particularly large in 1975 and subsequent years.

In judging the overall impact of such schedules on atmospheric PNA levels, the contribution of tailpipe emissions to total atmospheric loading must be estimated. In cities such as Los Angeles and Washington, D. C. and several other communities most of the atmospheric PNA can be associated with automobile emissions. The atmospheric levels in such communities average around 2 ug/$m^3$ for benzo(a)pyrene.[4] In highly industrialized communities in the eastern and southern U. S. with significant usage of coal, benzo(a)pyrene levels average from 4 to 10 ug/$m^3$ with several communities having levels averaging at or above 20 ug/$m^3$. Therefore, the automotive contribution can range from 10 to 50% in such coal burning areas and higher in non-coal burning or non-industrialized communities. A 50% increase in PNA emissions, assuming proportionality, may lead to an increase of about 1 ug/$m^3$ of benzo(a)pyrene, compared with present overall community levels of 2 to 20 ug/$m^3$.

There is a compensating factor even when increases in PNA emissions occur. As older higher-emission vehicles are removed from the roads, PNA emissions will decrease as indicated by the decrease in the reference schedule. Even with schedule N, this factor more than compensates for the increases in PNA emissions compared to the reference schedule after 1972. Even a 60% increase in 1980 in PNA emissions (schedule N, sub-model I) versus the reference schedule still results in a PNA emission level which is only one-third of the emission level in 1971 (reference schedule). The appropriate sub-model becomes significant in such cases, since sub-model II predicts a 25% rather than 60% increase in 1980 for schedule N. A resolution of the differences in experimental results on aromatics in fuel sensitivity of polynuclear aromatic hydrocarbons in exhaust is needed.

Phenols. Gross[2] reported on analyses for phenols in vehicle exhaust. Phenols are linearly related to fuel aromatic content at least in the 11 to 46% aromatic range. The phenol emissions from the 1970 vehicle tested were 70 to 75% as high as were the emissions from 1960 and 1968 vehicles. The concentration levels of phenols in exhaust are not sufficient to lead to atmospheric levels of concern. Phenols as other organic species may effect the carcinogenic potential of polynuclear aromatic hydrocarbons.

Photochemocal Reactivities. The term photochemical reactivity is a general term which refers to a number of individual chemical, physical or biological manifestations resulting from the reactions caused by ultraviolet irradiation in the 3000-4000 Å region of simple or complex mixtures of organic substances with nitric oxide and/or nitrogen dioxide. The manifestations include ozone, nitrogen dioxide, peroxyacyl nitrate (PAN), or aldehyde maximum concentrations or dosages (ppm x time), eye irritation response, plant damage and aerosol formation (visibility reduction). Other chemical effects such as rate of hydrocarbon reaction or nitrogen dioxide formation from nitric oxide are readily measured, but such effects are not of direct environmental concern in themselves. The intensity of these individual manifestations are not proportional to one another. For example, a single hydrocarbon or mixture of hydrocarbons compared to another hydrocarbon or mixture with nitrogen oxides when irradiated may produce large ozone yields but low eye irritation responses. Most individual olefinic or aromatic hydrocarbons when irraidated with nitrogen oxides do produce substantial intensities for one or more manifestations. Most paraffinic hydrocarbons and acetylene are much less reactive than olefins or aromatic hydrocarbons.

The reactions of these irradiated systems are sensitive to temperature, humidity, concentration, composition, and ratio of reactants, and added substances such as sulfur dioxide or carbon monoxide. Changes in composition of gasolines, emission mixtures or atmospheric samples do not produce as large variations as does the adjustment of concentration and ratio of reactants. Nevertheless, the effects of varying olefins or aromatic content for fuels on photochemical reactivity has been the subject of much experimental investigation.

Concern has been expressed that the removal of lead from gasoline will result in the need for higher aromatic content to which has been attributed a possibly higher photochemical reactivity. In practice, the increase in aromatics in gasoline must occur concurrently with reduction of olefins, paraffins or both fractions in the fuel. The paraffins are in part converted in the combustion process to move reactive olefins - ethylene, propylene, butenes. The net result is a complex balance of composition and reactivity in vehicle emissions which are not readily predicted from laboratory irradiations of simple mixtures. As a result, the present discussion will be concerned with the reactivities resulting from irradiation of complex hydrocarbon mixtures with nitrogen oxides, exhaust emissions and evaporative emissions.

Several current and past studies (Hurn and Davis[5], Dishart[6], Wigg, Campion and Peterson[7] provide a good basis on fuel-exhaust hydrocarbon relationships. Such relationships are needed in computation of photochemical reactivity. The results can be summarized as follows:

1. For both uncontrolled and device controlled vehicles utilizing leaded or non-leaded fuels, exhaust aromatic content is linearly related to fuel aromatic content. No effect can be shown of fuel olefin content on exhaust aromatic emissions.

2. Exhaust olefins decrease as fuel aromatics increase. The major portion of exhaust olefins are the cracked products from combustion (ethylene, propylene, butenes) not the unburned fuel olefins. Exhaust olefin content is linearly related to the sum of fuel olefin plus fuel paraffin content. Again the effects of control devices versus uncontrolled exhaust emissions along with leaded versus non-leaded fuels is minimal.

3. Increasing fuel aromatic content from 0 to 55% results in a decrease in total molar aldehyde emissions of about 10%. The

relationship between fuel aromatics and exhaust aromatic aldehydes is linear.

The above results make it possible to assume linear relationships in emissions within and among various vehicles types of 1967 and earlier, and up to 1975 model year. Emission tests on prototype vehicles indicate that the more reactive fuel and exhaust aromatics and olefins are removed in greater relative amounts than cracked products such as methane, ethylene and acetylene by catalytic devices and by thermal reactors.

Photochemical Reactivity - Oxidant - The Federal air quality standards are based on ozone or corrected oxidant measurements. No standards exist related to other photochemical reactivity manifestations such as eye irritation, visibility reduction, plant damage nor the chemical rate of reaction parameters. The corrected oxidant measurement involves correction for sulfur dioxide and nitrogen oxides. The net oxidant values resulting have ozone as the major constituent, but the smaller amounts of oxidants such as peroxyacyl nitrates (PAN + PPN) would also be included in the measurement. Therefore, laboratory smog chamber measurements of irradiated vehicle emissions or simulated vehicle emissions for ozone and peroxyacyl nitrates as a function of hydrocarbon emissions are most significant. Because of the differences in concentration - time relations in the atmosphere compared to the smog chambers, dosage values - PPM minute for the duration of the experiment usually 5 or 6 hours, are utilized rather than the peak concentration in the smog chamber.

In work reported recently (Sturn and Dimitriades[8]) irradiationcchamber measurements were made on emissions from a vehicle operated on four different leaded and non-leaded fuels of varying aromatic content. Results were obtained on both exhaust plus evaporative emissions (1/1) and evaporative emissions. The results are given in Table II. Fuel A, of 29% aromatic content and 99.5 RON is least reactive. But fuel C (leaded) of 22% aromatic content and 95.4 RON is not significantly less reactive than fuel B (lead-free) 45% aromatic content and 101.9 RON. Fuel D (lead-

free) of 31% aromatics is significantly more reactive than fuel B (lead-free) of 45% aromatic content while fuel A is less reactive than fuel C of lower aromatic content. Fuel D is more reactive than fuel C. Therefore, no consistent relationship exists between fuel aromatics and these measures of photochemical reactivity whether leaded or non-leaded fuels are compared.

In a more recent set of unpublished measurements[9] (Air Pollution Progress Report, June 30, 1971) from Bureau of Mines, Bartlesville Research Center reactivity measurements were obtained using 7 fuels in one vehicle to provide emissions irradiated in a smog chamber. The ozone, oxidant and peroxyacyl nitrate (PAN) results available are summarized in Table III. The reactivity values again do not vary with fuel aromatic content. The average exhaust reactivity of the 52% aromatic content fuel is within 1% of the average reactivity value for all 7 fuels. The reactivities of fuels 7003, 7005, and 7006 of 32, 28, 26% aromatic content are consistently higher than fuel 7011 of the high aromatic fuel. The reactivities of the evaporative emissions of the fuels containing 52% and 32% aromatics are at the low end of the highest aromatic content fuel 7011 is lower than the reactivities of all of the lower aromatic content fuels. The reactivities of the evaporative emissions increase with fuel olefin content rather than fuel aromatics.

In a recent study in the EPA laboratories[10] complex, hydrocarbon mixtures were irradiated with nitrogen oxides. The mixture simulated atmospheric hydrocarbon composition. The paraffin-acetylene fraction consisted of n-pentane, isopentane, 2-menthyl pentane, 2, 4-dimethyl pentane, 2, 2, 4-trimethyl pentane and acetylene. The olefin fraction consisted of ethylene, propylene, butene-1, cis-butene-2, 2-methyl-m-xylene, n-propylbenzene, see-butylbenzene and 1, 2, 4-trimethylbenzene. The proportions of each fraction were varied to determine the reactivity effects of replacement or addition of the three major hydrocarbon fractions. Part of the measurements are plotted in figures 1 and 2 for oxidant (corrected) and peroxyacyl nitrate (PAN) as a

function of olefin to aromatic content and of aromatic content and of aromatic to paraffin content. Substitution of aromatics for olefins cause consistent reduction in both oxidant and peroxyacyl nitrate dosages. A further reduction occurs as aromatics are largely replaced by paraffins. Although not plotted, replacement of olefins with paraffins also causes a substantial reduction in oxidant and peroxyacyl nitrate dosages.

All of these results clearly show that increase in aromatics in fuel should not be expected to lead to increases in oxidant or peroxyacyl nitrate dosages. Although not listed, the maximum oxidant concentrations also are insensitive to aromatic content of fuels.

Formaldehyde Dosage - Formaldehyde is one of the eye irritants associated with photochemical smog. Formaldehyde dosage decreased by 20% as aromatic content of the fuels utilized increased from 23 to 52% in the Bureau of Mines irradiations of vehicle exhaust emissions mixtures.[9]

Eye Irritation Response - Eye irritation responses of human panelists have been reported in several studies involving irradiation of exhaust emissions from vehicles utilizing fuels of varying hydrocarbon composition.

A significant reactivity parameter utilized for over 15 years is the eye irritation response of human panelists to irradiated auto exhaust or hydrocarbon-nitrogen oxide mixtures. One of the studies seeking to quantitate eye irritation response to fuel composition effects on vehicle exhaust were conducted by Schuck and co-workers[11] in 1958 utilizing four vehicles and five test fuels. The hydrocarbon to nitrogen oxide ratios and chamber residence times were varied by changes in engine operating conditions. The highest level of eye irritation was obtained by use of the olefinic fuel (52% olefin, 24% aromatic). The basis mix fuel (16% olefin, 22% aromatic) produced an exhaust which when irradiated caused less eye irritation than produced from the olefinic fuel, but more eye irritation than produced from the exhaust formed by use of an aromatic fuel (32% aromatic, 0.0%

olefin; 33.5% aromatic, 0.5% olefin) or a paraffinic fuel (97% paraffin, 3% aromatic). In several of the experiments only the higher eye irritation response of the olefinic fuel could be distinguished statistically from that produced from the other fuels. The eye irritation response produced from the aromatic and paraffin fuels could not be distinguished. During the same period Hamming, et al.[12] measured fuel composition effects on the reactivity of irradiated exhaust. The influence of olefin content of fuel was emphasized and a 22% increase in eye irritation index was reported to occur with an increase of olefin content by 25% (6 to 31% olefin content). An increase of the aromatic content of fuel 36% (2% to 38%) was required to produce 8% increase in eye irritation index.

Work done by Wilson and Co-workers[13] relating several photochemical reactivity parameters to fuel composition effects on exhaust including some eye irritation panel response measurements. Irradiated exhaust from use of a 55% aromatic fuel caused eye irritation with 10% greater severity than from a 25% aromatic fuel. When 0.75 ppm of sulfur dioxide was added to the exhaust, the irradiated exhaust from use of a 55% aromatic fuel caused eye irritation 90% more severe than from 25% aromatic fuel. This result was attributed to a reduction in eye irritation in the exhaust with higher olefin content (25% fuel aromatic content). Other measurements on this fuel with 0.1 ppm $SO_2$ added resulted in a 30% reduction in eye irritation. However, measurements with a 60% olefin - 40% aromatic-6 component mixture showed no effect of increasing $SO_2$ from 0.00 to 0.3 ppm. A mixture consisting of 7.5% aromatics, 0.5% olefins and the rest paraffinic upon irradiation with nitrogen oxide produced 30% less eye irritation with no $SO_2$.

While $SO_2$ does appear to have an effect on eye irritation of some hydrocarbon mixtures, it is not at all clear at present whether $SO_2$ at atmospheric levels around 0.1 ppm or less would interact with exhaust hydrocarbon mixtures having smaller shifts in composition that used in the work of Wilson, et al. to produce significant changes in eye irritation.

Eye irritation responses also were obtained in the work in EPA laboratories[10] on mixtures of the hydrocarbon fraction described earlier in this paper. The eye irritation indices of the panel responses are tabulated in Table IV. These mixtures represent the types of atmospheric composition which would result from very large changes in fuel usage. Therefore, the changes in eye irritation indices will be greater than those resulting from the smaller shifts in fuel composition involved in the Bonner and Moore fuel schedules.

A shift from a purely aromatic exhaust mixtures through an equal carbon ppm mixture (26 mole% aromatic, 74% mole% olefin) to a purely olefinic mixtur. causes no significant change upon irradiation in eye irritation index. Only when an appreciable fraction of paraffinic hydrocarbons are substituted for olefins and aromatics does a really significant shift in eye irritation index occur. Thus a mixture of the same carbon ppm level but containing a molar composition of 25 mole% aromatics, 27 mole% olefins and 48 mole% paraffins (mixture 4) does result upon irritation in 35 to 40% less eye irritation than mixtures of olefins and/or aromatics only. Based on the compositional relationships obtained by Wigg, Campion and Peterson,[7] this type of exhaust composition (mixture 4) would be expected from a fuel containing 45 to 50% aromatics. Changes in composition resulting in large variations in the proportions of olefins and aromatics (mixtures 5 and 6) with elimination of paraffins cause small downward shifts in eye irritation. If the contribution of the amount of paraffin present is considered additive, mixtures of 10 carbon ppm of olefin with 10 carbon ppm of paraffin (63 mole% olefin, 37 mole% paraffin) would have an eye irritation index of 1.40 (1.10 + 0.30). A mixture of 5 carbon ppm olefin, 5 carbon ppm aromatic and 10 carbon ppm paraffin (39% olefin, 14% aromatic, 47% paraffin) would have an eye irritation index of 1.35 (1.05 + 0.30). So shifts in which olefin ranges from 27 mole% to 63 mole% and aromatic from 0 mole% to 25 mole% compute to cause a $\pm$ 8% variation in eye irritation response.

A significant downward shift occurs again when the 10 carbon ppm total mixtures of olefins or olefins plus aromatics are substituted for by paraffins as in mixture 7. Substitution of 5 carbon ppm of olefin in mixture 6 by almost an equal amount of paraffin in mixture 7 with a small increase in aromatics causes a decrease in index of 25% in eye irritation index. The complete replacement of olefins or aromatics with paraffins in mixture 8 results in a mixture which upon irradiation causes one-quarter or less of eye irritation from mixtures 4, 5 or 6.

Similar results were obtained in mixtures irradiated with 0.5 ppm of nitrogen oxide. Again partial replacement of aromatic or olefin with paraffin causes a significant decrease in eye irritation response. However, a mixture of a high aromatic content (mixture 10) has the same eye irritation index, 0.80 units, as does mixture 11 with much less aromatic and a large increase in olefin content.

These results with simulated atmospheric mixtures fail to show: substantial effects on eye irritation of substituting aromatics for olefins. Only substitution of paraffins for olefins and aromatics can be predicted to cause large decreases in eye irritation in irradiated hydrocarbon - nitrogen oxide mixtures. Shifts of aromatics and olefins over ranges which are at the extremes for realistic gasoline composition changes are likely to cause eye irritation responses of about $\pm$10%. This result is consistant with the results of Hamming, et al,[12] and Wayne, 1962,[14] in which large increases in fuel olefins from 7 to 31% and fuel aromatics from 2% to 72% caused their eye irritation index to vary from 64 to 79 units or $\pm$ 7.5 units in 70 units.

Overall the results do suggest that extremely large increases in olefins or aromatics in gasoline so that lower reactivity paraffins and acetylene were substantially reduced could cause modest increases in eye irritation. However, the Wigg, et al,[7] relations clearly show within the range of 10 to 55% aromatics in fuel, increases in exhaust aromatics are largely compensated by a reduction in exhaust olefins. For example, at 20% fuel

aromatics, the exhaust mixture contains 10% aromatic and 33% olefins or a total of 43% olefins and aromatics, while for 30% fuel aromatics the exhaust mixture contains 15% aromatic 30% olefin or a total of 45% olefin and aromatics. Thus a 10% increase in fuel aromatics results in only 2% increase in exhaust aromatics plus olefins, resulting in only a small change in eye irritation potential.

Plant Damage - Damage to various species, particularly petunia, pinto bean, tobacco wrapper, and bluegrass has been obtained by irradiation of hydrocarbon-nitrogen oxide mixtures. The chemical species causing the damage are ozone, peroxyacyl nitrates and possibly alkyl hydroperoxides from certain aldehydes. The available measurements suggest the following order of decreasing plant damage potential by class of organic substance olefins aromatics aldehydes paraffins-acetylene (Altshuller[15]). The trend should correlate with the oxidant or ozone and peroxyacyl nitrate dosages discussed. As indicated, increase in aromatics with reduction of olefins in fuel result in no significant adverse effect of increased aromatics on these reactivity parameters. The reactivity of evaporative emissions is more depended on olefin than on aromatic content. The aliphatic aldehydes that produce plant damage upon irradiation are the products from the olefin not the aromatic content of exhaust. These comments are fully consistent with the one study in which fuel composition was considered as a parameter related to the plant damage potential of exhaust products. In the work done by Noble, et al[16] and Wayne,[14] much greater plant damage to bluegrass was obtained by irradiation of the exhaust from a highly olefinic fuel than from a highly aromatic fuel.

Based on the above considerations, an increase in the aromatic content of the fuel would not be expected to increase the plant damage potential of irradiated exhaust. Depending in part on the detailed composition of the aromatic fraction of the fuel, increase in aromatics in fuels could lead to a reduction in the plant damage potential of the irradiated exhaust and evaporative emissions.

Aerosol Formation - Olefins and alkylbenzenes when irradiated with nitrogen oxides and sulfur dioxide produce aerosols. Four carbon olefins and smaller produce only small amounts of aerosol compared to higher molecular weight olefins and alkylbenzenes. Aerosol formation is greatly increased with addition of sulfur dioxide to irradiated olefin-nitrogen oxide mixtures, but not to aromatic-nitrogen oxide mixtures. Paraffinic hydrocarbons and acetylene when irradiated with nitrogen oxides and sulfur dioxide produce very small amounts of aerosols. Wilson, Miller, and Levy,[17] demonstrated that the degree of stirring is critical. They also showed that binary hydrocarbon mixtures in which one or both hydrocarbons are aromatic produce much less aerosol than would be predicted from respective single-component experiments.

Earlier work by Schuck, et al,[11] on irradiated exhaust indicated olefinic fuels produced the greatest amount of aerosols. The work reported by Hamming and co-workers[12] suggested an increase in aerosols with increase in fuel aromatics. Wilson, et al,[17] investigated this problem using exhaust or exhaust plus evaporative losses with 0.1 ppm of added sulfur dioxide. Five leaded and unleaded fuels were used with an engine having leaded deposits. The primary aerosol formation was not related to fuel aromatics. Photochemically aerosols (secondary) formed in somewhat greater quantities as measured by light-scattering coefficient with increasing fuel aromatics. These results are complicated by the results for a fuel with 25% fuel aromatics which produced much more secondary aerosols than fuels containing 15 and 21% aromatics and as much aerosol as produced from fuels containing 48% and 55% aromatics. The secondary aerosols from irradiation of the two fuels averaging 18% aromatics produced 40% less aerosol than the two fuels averaging 52% aromatics. For total aerosols (primary plus secondary) the two low aromatic fuels produced 30% less aerosol than formed from the two high aromatic fuels. The results for fuels with the 25, 48, 55% aromatic contents could be interpreted as indicated in leveling off in aerosol formation between 25 and 55% fuel aromatics. In view of the difference in

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sensitivity of olefins and aromatics to sulfur dioxide the use of a range of sulfur dioxide contents might lead to differences in fuel composition effects also.

Computed Photochemical Reactivities - The previous discussion of photochemical reactivities has been based on experimental results on irradiated mixtures in smog chambers. Another approach is to compute reactivities from exhaust composition measurements and from a reactivity scale which assigns a reactivity value to each hydrocarbon class or sub-classes.

In the paper by Wigg, Campion and Peterson[7] the exhaust composition measurements were used to calculate photochemical reactivity by the composite reactivity scale developed by Altshuller[15, 18], which averages over a number of chemical, physical and biological smog manifestations. Using this scale, class rankings were obtained in which olefins, aromatics, and paraffins - acetylene-benzene were weighted 5.5, 4.5, and 0.5, respectively. The exhaust composition in change with fuel aromatic content was calculated as follows:

$$\text{Exhaust Alkylbenzenes (mole \% in exhaust)} = 0.49 \text{ Aromatic Content (Mole \% in fuel)}$$

$$\text{Exhaust Olefins (mole \% in exhaust)} = 39 - 0.3 \times \text{Aromatic Content (Mole \% in fuel)}$$

or

$$= 13 + 0.23 \text{ (Olefin + Paraffin content) (Mole \% in fuel)}$$

The reactivities are a linear summation of the product of exhaust composition multiplied by the reactivity factor. Based on this approach, the increase in reactivity with an increase in fuel aromatic content from 20 to 40% is 4%.

A similar computation was made which used the hydrocarbon subclasses. The result was an increase in specific exhaust reactivity of 7% for an increase in fuel aromatic content from 20 to 40%. The specific reactivity levels off and decreases above 40% because of the shift in internal composition of the aromatic fraction. The authors utilize a 7% decrease in hydrocarbon mass emissions as representing the effect of shifting from a leaded to unleaded fuel. Based on this correction, the two reactivity computations give a net change of -3% and 0%. Wiggs, et al,[7] conclude that the predicted impact of increased fuel aromaticity on photochemical reactivity is very small.

Dimitrades, Ecceston, and Hurn,[19] computed eye irritation from exhaust composition and eye irritation scales developed by Heuss and Glasson[20] and Altshuller[18]. Based on the two scales used to obtain comparing a 23% aromatic content fuel with a 50% aromatic content fuel, + 10%, + 1% increase; comparing another 23% aromatic content fuel with a 43% aromatic content fuel, 0%, + 11%; comparing the same 23% aromatic content fuel with a 36% aromatic content fuel, + 7% and 10%. The increases for the three sets of fuels compared averages overall for the two scales at 7% for fuel aromatic content increase of 20% (23% to 43%).

## Summary

The results discussed in this paper are summarized in Table V in which either the quantity of the pollutant emitted or the intensity of the photochemical effect observed with solar irradiation is related to an increase in fuel aromatic content on a per vehicle basis. These estimates do not include the compensation in effects of fuel aromatic increases resulting from the decrease in overall emissions reported to occur from substitution of unleaded deposits from lead-free fuel usage for the present lead deposits. This unleaded deposit effect has been found in most studies to reduce gaseous emissions and polynuclear aromatic hydrocarbon emissions. The cause of this deposit effect has not been isolated with respect to lead, phosphorus and base fuel characteristics.

As indicated in the previous discussion, the emissions for the vehicle population rather than single vehicles are of importance. Since emission factors vary with model years, the overall effect of a change in fuel aromatics depends on the aromatic content of each grade of fuel and the vehicle sub-population utilizing that grade of fuel. The emission factors decrease from 1.0 to approximately 0.02 for exhaust aromatics and olefins and probably for polynuclear aromatics in comparing controlled 1967 model year and earlier vehicles with 1975 model year vehicles. Even where positive effects occur (in some vehicle sub-populations) the overall effects can actually be negative or only slightly positive if the fuel aromatics are decreased in high emitter sub-populations and increased in low emitter sub-populations. As a result, schedule O in the Bonner and Moore Study[3] would lead to a small net decrease or no effect for polynuclear aromatic hydrocarbons and phenols through 1967 and no effect for photochemical reactivity. Schedule A results in no photochemical effect and a small change of ± 10% or less in emissions depending on the year by year schedule. For photochemical reactivity effects even a change of 5% in average aromatic hydrocarbon emissions averaged over the entire vehicle population which would correspond to an overall increase of 10% in fuel aromatics could barely be detected for any manifestation with the possible exception of aerosol formation. Both schedules A and O require increases of less than 10% in the pool fuel aromatic content. Additional compensation results from distribution of the increases in fuel aromatics to the low emitting vehicles.

If an ambient air standard at or near 2 $\mu g/m^3$ annual or seasonal average is selected, schedule A will not provide adequate reductions of lead until into the 1980's. Schedule O will provide reductions so that cities at or below 4 $\mu g/m^3$ will be at or within the Standard by 1974, cities at or below 5 $\mu g/m^3$ will be at or within the Standard by 1975 and cities at or below 6 $\mu g/m^3$ will be at or within the Standard by 1977. Schedule N would achieve needed ambient air standards by 1974. However, this more severe schedule would lend to appreciable increases in atmospheric levels of polynuclear

MAR 8 RECD

TO: Recipients of proposed regulations affecting the use of lead and phosphorus additives in motor vechile gasoline

FROM: Environmental Protection Agency

The enclosed paper is referenced in the proposed regulations, which have already been sent to you. It had not been reproduced in time for mailing with the proposed regulations. It is now being mailed to all persons and organizations that were sent copies of the proposed regulations.

aromatic hydrocarbons, phenols and perhaps organic aerosols. Schedule N is somewhat more costly in terms of cost per gallon to the motorist and does induce a business cycle in the construction industry.

Recommendation

Either schedule A or O in the Banner and Moore study would achieve most of the objectives listed at the beginning of this discussion. Schedule O, but not schedule A would come close to achieving acceptable atmospheric levels of lead particulate material in a reasonable time interval. Neither schedule A or O should result in any significant adverse effects on emissions or photochemical reactivity because of changes in fuel composition. Other schedules similar to A and O could be selected which should be equally acceptable.

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Table I. CALCULATION OF IMPACT OF BONNER AND MOORE (1971 STUDY) LEAD-REDUCTION SCHEDULE ON POLYNUCLEAR AROMATIC TAILPIPE EMISSIONS FROM PASSENGER VEHICLES

| | Year | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1971 | 1972 | 1973 | 1974 | 1975 | 1976 | 1980 |
| | Baseline[a] | | | | | | |
| | 71.0 | 63.7 | 56.4 | 49.8 | 42.3 | 35.5 | 15.0 |
| Schedule | Change from baseline, % | | | | | | |
| 0 - Submodel I[b] | - | -13 | - 7 | -12 | - 2 | - 1 | +22 |
| 0 - Submodel II[c] | - | -13 | - 9 | -11 | - 8 | - 6 | +13 |
| N - Submodel I[b] | - | +16 | +15 | +22 | +56 | +44 | +60 |
| N - Submodel II[c] | - | +12 | +10 | +12 | +38 | +26 | +25 |
| A - Submodel I[b] | +10 | - | - | - | - | -14 | - 6 |
| A - Submodel II[c] | + 9 | - | - | - | - | -14 | - 9 |

[a]Baseline reference number normalized to 100% vehicles as per U.S. vehicle distribution and to relative emission factors.

[b]Linear aromatic fuel content effect on PNA emissions for 1974 and earlier models.

[c]Linear aromatic fuel content effect on PNA emissions for 1967 and earlier models and no aromatic fuel content effect on PNA emissions for 1968 and later models.

Table II. REACTIVITY OF FUELS WITH DIFFERENT AROMATIC CONTENTS - IRRADIATED EXHAUST PLUS EVAPORATIVE EMISSIONS AND EVAPORATIVE EMISSIONS SEPARATELY

| Concentration of reactants | Type of sample | Fuel designation/% aromatic content | | | |
|---|---|---|---|---|---|
| | | Fuel C/ 22% | Fuel A/ 29% | Fuel D/ 31% | Fuel B/ 45% |
| $HC/NO_x$: 6 ppm C/1 ppm | | | | | |
| 1. Oxidant (KI), ppm-min. | Exhaust + evaporation | 60 | 28 | 70 | 61 |
| 2. PAN + PPN, ppm-min. | | 8.0 | 5.7 | 11.0 | 9.4 |
| 1. Oxidant (KI), ppm-min. | Evaporation | 5.6 | - | 13.8 | 3.1 |
| 2. PAN + PPN, ppm-min. | | 2.1 | 1.7 | 4.0 | 1.7 |
| $HC/NO_x$: 3 ppm C/0.5 ppm | | | | | |
| 1. Oxidant (KI), ppm-min. | Exhaust + evaporation | 65 | 45 | 75 | 71 |
| 2. PAN + PPN, ppm-min. | | 5.4 | 4.7 | 8.3 | 7.6 |
| 1. Oxidant (KI), ppm-min. | Evaporation | 19.6 | - | 27.1 | 15.5 |
| 2. PAN + PPN, ppm-min. | | 1.7 | 1.6 | 3.0 | 1.4 |

Table III. REACTIVITY OF FUELS WITH DIFFERENT AROMATIC CONTENTS - IRRADIATED EXHAUST AND EVAPORATIVE EMISSIONS

| Concentration of reactants | Type of sample | Fuel designation/% aromatic content | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 7002/ 23% A | 7004/ 24% A | 7006/ 26% A | 7007/ 27% A | 7005/ 28% A | 7003/ 32% A | 7011/ 52% A |
| $HC/NO_x$: 6/ppm C/1 ppm | | | | | | | | |
| 1. Oxidant (KI), ppm-min. | Exhaust | 152 | 162 | 163 | 138 | 174 | 165 | 163 |
| 2. Ozone (chemiluminescence), ppm-min. | | 145 | 152 | 160 | 140 | 157 | 160 | 157 |
| 3. PAN + PPN, ppm-min. | | 19.2 | 19.8 | 21.3 | 16.0 | 23.2 | 22.1 | 20.7 |
| 1. Oxidant (KI), ppm-min. | Evaporation | 11.9 | 5.4 | 10.6 | 5.5 | 17.7 | 4.8 | 1.7 |
| 2. PAN, ppm-min. | | 3.7 | 2.1 | 3.6 | 2.0 | 4.5 | 2.5 | 1.6 |
| $HC/NO_x$: 3/ppm C/1 ppm | | | | | | | | |
| 1. Oxidant (KI), ppm-min. | Exhaust | 96 | 99 | 107 | 91 | 110 | 98 | 103 |
| 2. Ozone (chemiluminescence), ppm-min. | | 93 | 100 | 104 | 95 | 107 | 97 | 98 |
| 3. PAN + PPN, ppm-min. | | 8.6 | 9.2 | 9.8 | 8.3 | 10.4 | 10.0 | 9.2 |

Table IV. EYE IRRITATION INDEX FOR VARIOUS MIXTURES OF IRRADIATED HYDROCARBONS AND $NO_x$

| Mixture number | Aromatics, ppm C/mole % | Olefin, ppm C/mole % | Paraffin, ppm C/mole % | $NO_x$, ppm | Eye irritation index |
|---|---|---|---|---|---|
| 1 | 20 /100 | 0 / 0 | 0 / 0 | 1 | 1.95 |
| 2 | 0 / 0 | 20 /100 | 0 / 0 | 1 | 1.90 |
| 3 | 10 / 26 | 10 / 74 | 0 / 0 | 1 | 1.90 |
| 4 | 8 / 25 | 3 / 27 | 9 / 48 | 1 | 1.20 |
| 5 | 0 / 0 | 10 /100 | 0 / 0 | 1 | 1.10 |
| 6 | 5 / 26 | 5 / 74 | 0 / 0 | 1 | 1.05 |
| 7 | 5.5 / 41 | 0 / 0 | 4.5/ 59 | 1 | 0.89 |
| 8 | 0 / 0 | 0 / 0 | 10 /100 | 1 | 0.30 |
| 9 | 5 / 26 | 5 / 74 | 0 / 0 | 0.5 | 1.02 |
| 10 | 5.25/ 41 | 0 / 0 | 4.5/ 59 | 0.5 | 0.80 |
| 11 | 2 / 11 | 1.5/ 25 | 6.5/ 64 | 0.5 | 0.78 |
| 12 | 0 / 0 | 0 / 0 | 10 /100 | 0.5 | 0.32 |

Table V. POLLUTION EFFECTS RESULTING FROM 10% INCREASE IN FUEL AROMATIC CONTENT PER VEHICLE

| Substance emitted or effect observed | Probable result of 10% increase in fuel aromatic content per vehicle |
|---|---|
| Tailpipe emissions | |
| Polynuclear aromatic hydrocarbons | Linear increase up to 1968 (2) model or 1975 model vehicles |
| Phenols | Linear increase up to 1970 model vehicles-unknown on later models |
| Aromatic hydrocarbons (gasoline fraction) | Linear increase up to 1975 model vehicles |
| Olefins | Approximately linear decrease above 10% fuel aromatic content |
| Photochemical reactivity | |
| Ozone or oxidant | No increase overall and decrease for evaporative loss contribution |
| Peroxyacyl nitrate (PAN) | No increase overall and decrease for evaporative loss continuation |
| Formaldehyde and other aldehydes | Decreases with increase in fuel aromatic |
| Eye irritation | 2 to 5% increase |
| Aerosol formation | 10% increase (perhaps occurs only below 25% fuel aromatic) |
| Plant damage | No increase or possible decrease |
| Averaged overall of above manifestations | Very small or none (within ±5% change) |

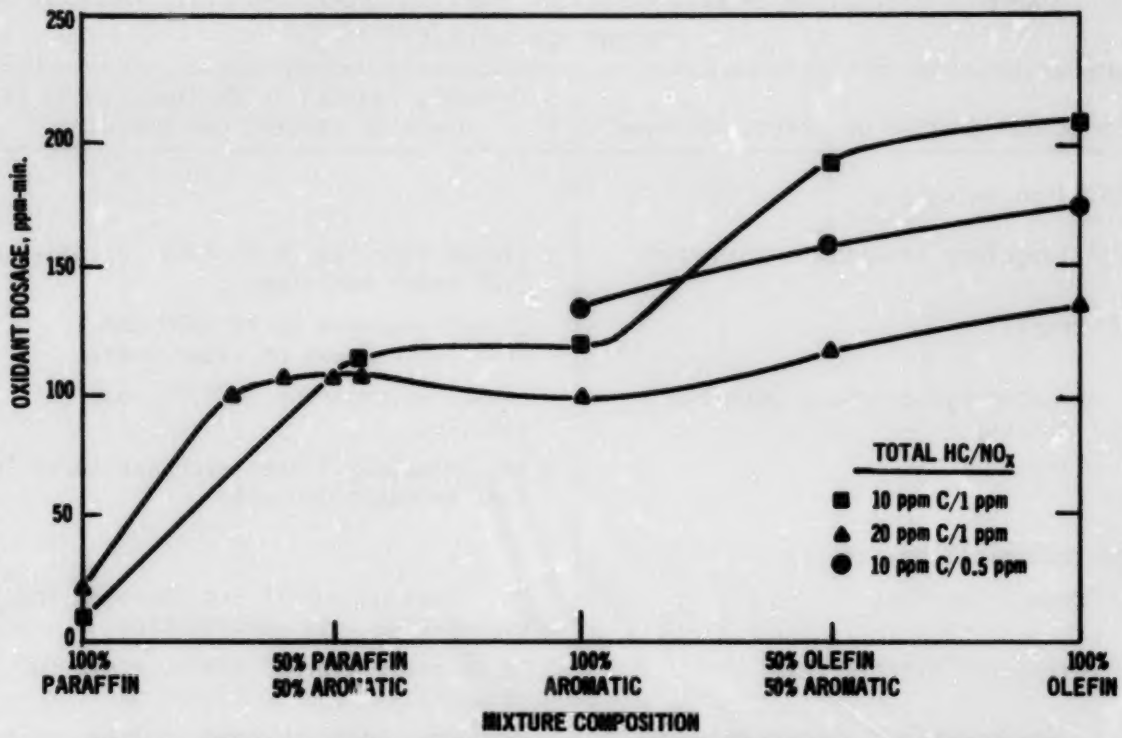


Figure 1. Effect of paraffin, olefin, aromatic mixture concentration on oxidant dosage.

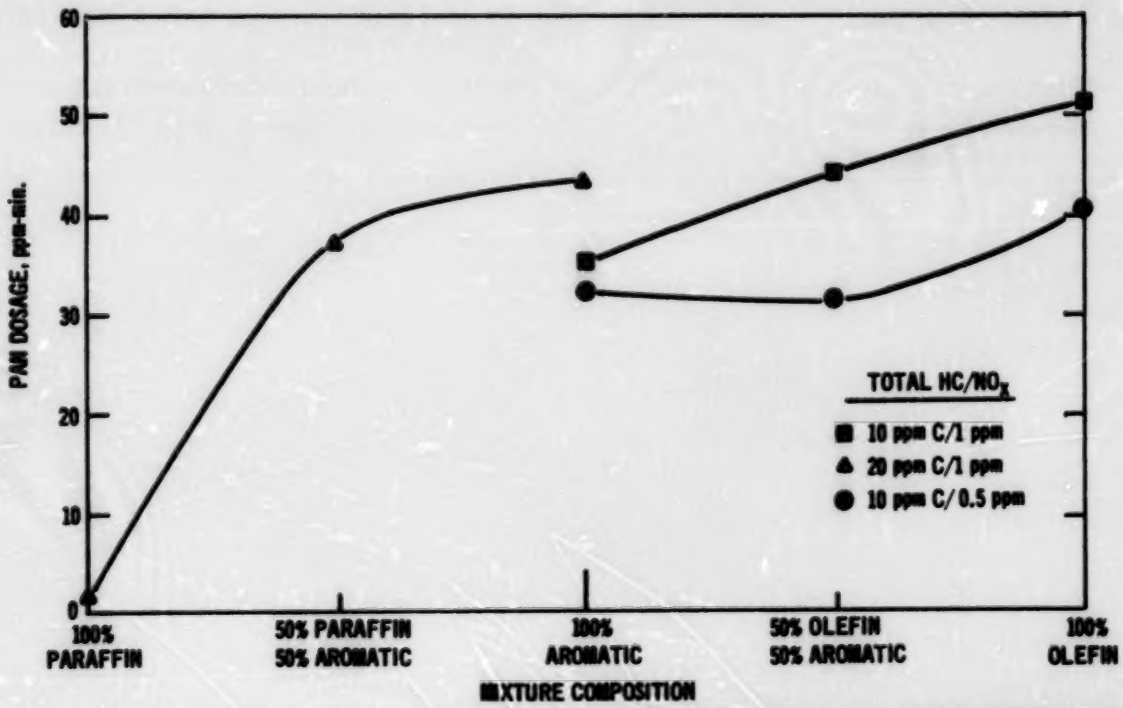


Figure 2. Effect of paraffin, olefin, aromatic mixture composition on peroxyacyl nitrate (PAN) dosage